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# **UNITED STATES PATENT APPLICATION FOR GRANT OF LETTERS PATENT**

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## **Installation and Method for the Purification of an Aqueous Effluent by Means of Oxidation and Membrane Filtration**

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INSTALLATION AND PROCESS FOR THE PURIFICATION OF AN  
AQUEOUS EFFLUENT BY MEANS OF OXIDATION AND MEMBRANE  
FILTRATION

The subject of the invention is the purification of aqueous effluents and it is particularly but not exclusively applicable to:

- treatment of industrial or domestic waste water;
- 5    - treatment of tip leached products (percolates);
- treatment of surface water to make it drinkable;
- depollution treatment of ground water;
- treatment of membrane filtration concentrates.

The main purpose of treatments for the  
10   purification of aqueous effluents is to eliminate organic material contained in these effluents and that is not easily biodegradable. Several methods may be used to achieve this objective.

It is thus known that effluents can be filtered on  
15   an adsorbent material such as activated carbon that is capable of retaining the organic material contained in them. Such a technique has the major disadvantage that it requires large quantities of adsorbent material for a given quantity of organic material to be eliminated,

and therefore can be very expensive. Regeneration of the adsorbent material itself is expensive.

Other processes use membrane filtration such as a microfiltration, ultrafiltration, nanofiltration or  
5 inverse osmosis membrane. Apart from the fact that they are also relatively expensive, such processes also have the disadvantage that they concentrate rather than destroy the polluting organic material. Therefore, this recuperated organic material then has to be degraded,  
10 usually by incineration.

Even other processes for elimination of organic material use a step consisting of flocculating the organic material, by adding one or more coagulating compounds in the treated effluents. These coagulating  
15 compounds may be mineral compounds for example such as polyaluminium chloride, alumina sulphate or ferric chloride or organic compounds for example such as cationic polymers. Coagulated flocs formed from organic material can then be eliminated by settlement.

20 Such processes have the major disadvantage that they produce large quantities of sludge that is a by product difficult to be eliminated. It will be noted that according to one improved coagulation - flocculation - settlement process, the flocculation  
25 step may be combined with oxidation by the introduction of Fenton's reagent ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ) into the effluent. Although the quantities of sludge produced during the use of such a process are much lower than in the case of a conventional flocculation process, they are  
30 nevertheless very large.

Finally, some aqueous effluent purification processes use a step in which the organic material is highly oxidised by a powerful oxidant (for example such as ozone, chlorine, chlorine dioxide) or a powerful  
5 oxidising system (for example such as ozone / UV, hydrogen peroxide ozone, hydrogen peroxide / UV). Oxidation facilitates degradation of organic molecules into smaller and more easily biodegradable molecules.

Ozone is the most attractive oxidant of the  
10 oxidising products conventionally used to oxidise organic material since, under some conditions of use, it is capable of completely destroying organic material by "mineralising" it into carbon dioxide and mineral salts. Furthermore, ozone enables radical reactions  
15 involving the OH free radical that provides a means of very strongly oxidising the organic material when it is applied to a basic pH or in combination with hydrogen peroxide or with ultraviolet radiation (the oxidoreduction potential of hydrogen peroxide is 1.6  
20 volts, the corresponding values for ozone and the OH radical are 2.07 and 2.7 respectively).

Therefore processes using oxidation provide a means of destroying the polluting organic material contained in the aqueous effluents rather than simply  
25 concentrating it as is the case with filtration processes, or separating it from the aqueous phase as is the case with coagulation - flocculation - settlement processes.

However, such processes have the economic  
30 disadvantage that they require relatively large

quantities of oxidising products to treat a given quantity of effluents.

The purpose of the invention is to provide a method for the purification of aqueous effluents including an optimised oxidation step, in other words a step in which the quantity of oxidising product necessary to treat a given volume of effluents will be less than in conventional oxidation techniques.

Such a process could be used to purify water containing large quantities of organic material, for example such as some industrial effluents or tip leached products, in other words water that has flowed through stored waste. These effluents are typically characterised by a very large content of organic material that is not easily biodegradable. Conventionally, these tip leached products have a BOD<sub>5</sub>/COD ratio often less than 0.1 leading to a very low biodegradability (BOD<sub>5</sub> represents the "Biological Oxygen Demand" of the effluent and defines the total quantity of organic material present in it). Therefore, it is difficult to purify such effluents because the only way of eliminating the organic materials from them is to use expensive treatment processes. In particular, in the past it has been impossible to consider purifying tip leached products using techniques involving powerful oxidants with reasonable treatment costs.

Another purpose of the invention is to provide a purification installation using small quantities of product compared with existing techniques according to the state of the art.

These and other purposes that will appear later are achieved using a purification installation for an aqueous effluent containing organic material of the type including at least one reaction vessel with at least one inlet of the said effluent, at least one outlet of the said effluent and at least one vent and injection means for at least one oxidising gas, the said reaction vessel containing a bed of a material capable of catalysing the oxidation reaction of the said organic material of the said effluent and / or adsorbing this organic material. According to the invention, the said reaction vessel also includes an immersed membrane filtration device and the said reaction vessel defines a single chamber including oxidation and filtration treatments of the said effluent, the said chamber being designed such that the said effluent and the said oxidising gas are injected in counter-current towards the said bed of catalyst material and then towards the said membrane filtration device.

Therefore, the invention clearly proposes a solution to combine several treatments inside a single compartment.

It will be understood that such integration offers a large number of advantages, including:

- reduction of operating costs related to filtration of the catalyst and / or adsorbent material, and putting it into suspension;
- economic saving due to elimination of structures and accessories;

- space saving induced by manufacturing of a more compact reaction vessel;
- simplification of the hydraulic system, and the use of less equipment.

5       The result of this integration according to the invention is a genuinely synergetic effluent treatment combination.

          The oxidising gas performs several functions in the installation according to the invention due to  
10 combining of treatment means like those defined above, in a single chamber.

          Firstly, the oxidising gas obviously performs a degradation function of organic materials dissolved in the effluent to be treated.

15       The oxidising gas performs a second function which is to hold the said material in suspension in the reaction vessel, which optimises the action of the reaction vessel.

          The oxidising gas performs another function which  
20 is to limit clogging of membranes of the filtration device due to the mechanical action of the gas on the membranes that in particular improves the effluent flow.

          Note that combining of the means of injection of  
25 an oxidising gas such as ozone and a membrane filtration device in the same reaction vessel according to the invention is a method that is contradictory to conventional practices that consist of using two separate tanks to separate the oxidation treatment and  
30 the membrane device, ozone (usually used as an

oxidising gas) being considered by those skilled in the art as being a membrane degradation source.

Surprisingly, the Applicant has observed that integration of oxidising and membrane filtration treatments in the same reaction vessel does not cause any degradation of membranes by ozone after oxidation of the refractory organic materials of the effluent. On the contrary, ozone contributes to limiting clogging of membranes, combining the mechanical action of gas bubbles and possibly the oxidising action on the clogging organic material present on the surface of the membrane, thus increasing the membrane cycle durations.

Therefore under optimum operating conditions, this action of ozone or more generally of the oxidising gas on the membranes is much more efficient than if a simple aeration of the membranes is done by injection of air or oxygen injected at the membranes.

Therefore, the invention is particularly effective and economic compared with the traditional method that would have led those skilled in the art to use two tanks: one for oxidation by ozone possibly in the presence of a catalyst, the effluent, the other tank for membrane filtration of the oxidised effluent, this second tank being provided with an aeration system specific to the membranes. Furthermore, this type of installation would result in the catalyst without ozone, if any, to saturate in the second tank, which could obviously mean that this catalyst might no longer be able to perform its role in the first tank when it is reinjected into it.



Furthermore, the installation according to the invention provides a means of regenerating the catalyst and / or adsorbent material directly in the reaction vessel, this regeneration advantageously taking place  
5 continuously.

According to one advantageous solution, the said material consists of a solid mineral material with a capacity for adsorption of organic materials, preferably doped in metallic substances.

10 The result is a particularly efficient and active bed of material since it optimises the oxidation action of the oxidising gas and retains a large fraction of the organic materials in the effluent within it.

Advantageously, the said material is present in  
15 the said reaction vessel in the form of a fluidised bed. In this case, the size grading of the said catalyst is preferably less than 100  $\mu\text{m}$  and preferably between about 10 nm and about 40  $\mu\text{m}$ .

According to one preferred solution, the said  
20 material comprises at least one material belonging to the following group:

- alumina;
- titanium;
- coal;
- 25 - activated carbon;
- polymetallic oxides.

According to a first variant embodiment, the membranes are micro-filtration membranes.

According to a second variant embodiment, the  
30 membranes are ultra-filtration membranes.

According to a third variant embodiment, the membranes are nano-filtration membranes.

One of these variant embodiments will be adopted depending on the required objective, for example this  
5 objective could be to obtain a simple separation of the material and the treated effluent, with treatment of undesirable substances.

Furthermore, according to one first embodiment, the membranes are of the mineral type.

10 According to a second embodiment, the membranes are of the organic type.

Advantageously, the said material forms a pre-layer on the surface of the said membrane filtration device.

15 The cake thus formed by the material on the surface of the membrane tends to significantly improve filtration and treatment performances of the corresponding membrane.

Preferably, the said oxidising gas comprises at  
20 least one of the oxidants belonging to the following group:

- air;
- ozone;
- ozoned air;
- 25 - nitrogen oxides;
- oxygen.

Ozone in particular could be chosen as a powerful oxidant that can give rise to strongly oxidising free radicals and allow decomposition of the organic  
30 material, either by transforming it into biodegradable materials or by mineralising it into carbon dioxide and

mineral salts. Other oxidants like that mentioned above could be considered by those skilled in the art.

According to one advantageous solution, the installation includes means of adding  $H_2O_2$  into the  
5 said reaction vessel.

This addition of  $H_2O_2$  can be made continuously or sequentially, its oxidising power possibly combining with that of ozone.

According to another characteristic, the  
10 installation comprises a recirculation loop of the said effluent in the said reaction vessel.

In this way, a contact time can be maintained between the effluent and the reagents within the reaction vessel while enabling a fairly high effluent  
15 flow.

In this way, the effluent treatment time within the reaction vessel can be increased if necessary.

Preferably, the said reaction vessel is made in the form of a column with no mechanical stirring.

20 The invention also relates to a process implemented using the installation that has just been described and characterised in that the said oxidising gas is added continuously into the said reaction vessel.

25 According to one preferred solution, the contact time between the said effluent and the said material is between about 5 minutes and about 3 hours, this duration preferably being between about 30 minutes and about 60 minutes.

30 Advantageously, the process comprises a step to re-circulate gas from the reaction vessel vent.

Preferably, the filtration step is performed by suction in external - internal configuration.

This step is advantageously done with a suction pressure of less than about 1 bar and preferably a  
5 suction pressure between 0.1 bars and about 0.8 bars.

Other characteristics and advantages of the invention will become clearer after reading the following description of a preferred embodiment of the  
10 installation according to the invention given as an illustrative and non-limitative example, with reference to the single Figure 1 that is a diagrammatic view of an installation according to the invention.

As illustrated in Figure 1, the installation comprises a reaction vessel 1 with an inlet pipe 9 for  
15 the effluent to be treated, an outlet pipe 10 for the treated effluent, a vent 5 in its upper part to be used for evacuation of gases and means 6 for recirculation of this gas at the bottom of the reaction vessel.

The installation also comprises means 2 for  
20 continuous injection of ozone into the reaction vessel that also contains a material 3 in the form of a fluidised bed.

A membrane filtration device 4 is also integrated into the reaction vessel 1.

25 Therefore in this way, the reaction vessel 1 defines a single chamber that includes effluent oxidation and filtration treatments, this single chamber being designed according to the invention such that the effluent and the oxidising gas (in fact ozone)  
30 is injected in counter-current towards the bed of

catalyst material 3 and then the filtration membranes 4.

Note that this reaction vessel is made in the form of a column with no mechanical stirring, effluent and 5 the oxidising gas being injected at the bottom of the column.

For example, the means 2 of injecting the oxidising gas consist of an emulsifier (also called a vacuum jar or hydroinjector). It is also possible to 10 use "Venturi" type emulsion equipment or any other apparatus for the formation of oxidising gas micro-bubbles in the liquid to be treated.

The material used to improve the reactivity of ozone is a mineral solid powder material present in the 15 reaction vessel in a proportion between 0.5 g/l and 50 g/l.

In this embodiment, this catalyst material is boehmite alumina ( $\gamma$   $\text{Al}_2\text{O}_3$ ) calcined at a temperature of less than 600°C. Note that boehmite alumina can be used 20 pure or in a form enriched in metallic substances (particularly in order to increase its capacity for adsorption of organic materials).

Furthermore, the catalyst material is finely divided such that the diameter of its particles is less 25 than 50  $\mu\text{m}$  (preferably, the diameter of the particles is about 30  $\mu\text{m}$ ), therefore the catalyst has a very high exchange surface area enabling adsorption of most organic materials in the effluent.

Furthermore, the catalyst particles contained in 30 the effluent are separated by using the membrane filtration device 4, made using membranes in which the

pore dimensions are preferably less than 0.1  $\mu\text{m}$ . These membranes are preferably made from ceramic or an organic polymer resistant to ozone.

Note that the membranes used may be micro-  
5 filtration membranes, ultra-filtration or nano-filtration membranes, depending particularly on the dimension of the catalyst particles.

Note also that the transition between the fluidised bed of the catalyst material 3 and the  
10 membranes 4 is such that the catalyst forms a pre-layer on the surface of membranes 4.

According to this embodiment, the effluent is filtered by suction in an external - internal configuration, using a pump 8 installed on the  
15 evacuation pipe 10; the said pump is used to obtain a suction pressure of about 0.8 bars.

Furthermore, a re-circulation loop 7 of the effluent is provided, by which the effluent is continuously (or semi-continuously according to another  
20 possible embodiment) recirculated in the reaction vessel. There is also a recirculation loop 6 for gases output from the vent 5.

Other embodiments or improvements are obviously possible, particularly by providing means of adding  
25  $\text{H}_2\text{O}_2$  as the only oxidant or combined with ozone in the reaction vessel.

We will now describe two tests carried out with the installation according to the invention.

The effluent to be treated in these tests was  
30 dirty water produced by the cosmetic industry after having been subjected to a biological pre-treatment.

Test in batch mode

A first series of tests is carried out in batch mode. Five litres of effluent are added into the reaction vessel. The effluent is oxidised in this reaction vessel into which ozone is injected continuously, the treated water being separated from the catalyst ( $\gamma$   $\text{Al}_2\text{O}_3$ ) using immersed micro-filtration membranes, the permeate being recirculated continuously in the reaction vessel.

In a first test, it is planned to treat an effluent with a COD (Chemical Oxygen Demand) of 213 mg/l and a TOC (Total Organic Carbon) of 75.8 mg/l, with a recirculated permeate flow of 10 l/h and an exposure time of 60 min. The treatment performed is ozone alone (without catalyst), the ozone being injected at a rate of 4.6 g of  $\text{O}_3$ /g of COD.

The results of this first test are as follows:

- final COD: 74.8 mg/l, namely a reduction of 64.9%
- final TOC: 34.1 mg/l, namely a reduction of 55%
- quantity of  $\text{O}_3$  consumed / TOC eliminated: 8.4.

In a second test, it is planned to treat an effluent with a COD (Chemical Oxygen Demand) of 181 mg/l and a TOC (Total Organic Carbon) of 61.4 mg/l, with a recirculated permeate flow of 10 l/h and an exposure time of 60 min. The treatment performed is a treatment with ozone in the presence of 20 g of catalyst per litre, the ozone being injected at a rate of 4.7 g of  $\text{O}_3$ /g of COD;

The results of this second test are as follows:

- final COD: 47.7 mg/l, namely a reduction of 73.6%

- final TOC: 19.9 mg/l, namely a reduction of 67.6%

5        - quantity O<sub>3</sub> consumed/TOC eliminated: 6.3.

These first tests clearly indicate that the catalysed oxidation followed by a membrane filtration in an installation according to the invention gives a better reduction both for COD and for TOC, compared  
10 with a treatment with ozone alone, and the ozone consumption is lower.

#### Tests in continuous mode

A second series of tests is carried out  
15 continuously. An effluent to be treated is injected into the reaction vessel at a flow rate of 10 l/h. The effluent is oxidised in this reaction vessel in which ozone is injected continuously, treated water being separated from the catalyst ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) using immersed  
20 micro-filtration membranes, the permeate not being recirculated in the reaction vessel, unlike in semi-continuous mode.

In a first test, it is planned to treat an effluent with a COD (Chemical Oxygen Demand) of  
25 185 mg/l with a flow of 10 l/h and an exposure time of 2 h. The treatment performed is a treatment with ozone alone (with no catalyst), the ozone being injected with a content of 3.8 g of O<sub>3</sub>/g of COD.

The results of this test are as follows:

30        - final COD: 104 mg/l, namely a reduction of 43.8%



- final TOC: 45.5 mg/l, namely a reduction of 35.7%

- quantity O<sub>3</sub> consumed/TOC eliminated: 11.1.

In a second test, it is planned to treat an effluent with a COD (Chemical Oxygen Demand) of 200 mg/l and a TOC (Total Organic Carbon) of 69.2 mg/l, with an exposure time of 48 h. The treatment performed is a treatment with ozone alone in the presence of 20 g of catalyst per litre, the ozone being injected at a rate of 4.2 g of O<sub>3</sub>/g of COD;

The results of this second test are as follows:

- final COD: 100 mg/l, namely a reduction of 50%

- final TOC: 40 mg/l, namely a reduction of 42.2%

- quantity O<sub>3</sub> consumed/TOC eliminated: 9.9.

In a third test, it is planned to treat an effluent with a COD (Chemical Oxygen Demand) of 200 mg/l, with an exposure time of 5 h. The treatment performed is an ozone treatment in the presence of 20 g of catalyst per litre, with added H<sub>2</sub>O<sub>2</sub>, the ozone being injected at a rate of 5.9 g of O<sub>3</sub>/g of COD;

The results of this third test are as follows:

- final COD: 72 mg/l, namely a reduction of 64%

- final TOC: 24.4 mg/l, namely a reduction of 64.7%

- quantity O<sub>3</sub> consumed/TOC eliminated: 9.1.

These tests show that the process and the installation according to the invention can give very good results compared with other treatments.